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STRUCTURAL INSTABILITY OF ARGILLACEOUS MATERIAL

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Some specifics of the structural instability of argillaceous materials and its effect on the properties of ceramics are considered. The effect of autoclave treatment on the dispersion processes in clays and kaolins is considered. It is demonstrated that controlled formation of the properties of the material at the stage of pretreatment lowers the degree of nonequilibrium of the processes in firing and leads to a higher-quality end product.

Instability in product quality can be due to different causes, such as fluctuations in the chemical and mineralogical composition, the instability of structure and phase composition of initial materials, and structural variations occurring in the synthesis of finished products. In the opinion of the authors in [1], it is possible to stabilize the process itself and the properties of the product by optimizing the system at the points of its instability and decreasing the degree of nonequilibrium of the process. The structural instability of the materials can have an especially significant effect on the nonequilibrium of processes.

Nearly all clay-forming materials exist in a crystalline state, which is frequently metastable. The crystallized lattice of such minerals can change radically under the effect of temperature, medium, pressure, etc. Structural instability or stability of the crystall lattice may arise either at the stage of rock formation or at the stage of preliminary treatment (thermal and technological prehistory).

The possibility of controlling the firing processes taking into account the genesis of rocks is shown in several publications, including [2, 3]. Another direction making it possible to improve the quality of argillaceous materials and increase the process efficiency is the use of rather simple techniques, such as natural treatment (estivation, freezing through), intense mechanical treatment and kneading of clay on clay-processing machines (runners, rollers, clay mills), aging of mechanically treated clays, steam treatment of clay, etc. [4, 5]. In such cases we are actually dealing with an artificial implementation of processes that are typical of diagenesis. Some petrologists believe that clay minerals are prone to modifications and soon adapt themselves to a new medium. In the case of erosion and outcrop of rocks, further modifications (diagenesis) take place. There is no unique opinion on the process of diagenesis in argillaceous materials; on the contrary, opposite opinions exist:

– argillaceous materials are sensitive to sedimentation; thus, kaolinite clays getting into a marine environment are transformed into illites and chlorites, and montmorillonites transform into chlorites;

– clay minerals are regarded as inert and behave like any other detrital rocks; the only modification recognized by supporters of this view is secondary absorption of cations in a marine environment, which, however, does not modify the main structural lattice of argillaceous minerals.

Important results were obtained by P. P. Budnikov in the study of processes that occur in argillaceous minerals under hydrothermal treatment [6].

Autoclave treatment (along with firing) can be an effective way to control the structure and properties of clay. In these conditions, when the mobility of the structure is maximal, the crystall lattice stresses relax. A manifestation of a structural transformation is the process of dispersion of particles.

We investigated several argillaceous materials: clays from the Gorodishchenskoe (sandy clay of mainly nontronite composition), Lukoshkinskoe, and Veselovskoe (kaolinite-hydromica clays) deposits, and kaolin from the Prosyanovskoe and Glukhovetskoe deposits. The chemical compositions of the materials are listed in Table 1.

The autoclave (steaming) treatment of argillaceous samples was carried out at a steam pressure of 1.0 MPa for 6 h. In this case the mineralogical composition (according to x-ray phase analysis) did not change. The average size of clay particles before and after autoclave treatment was determined using microscope analysis. Based on this analysis, the dispersion coefficient was calculated as the ratio of the average particle size of the initial material to the particle size of material treated in an autoclave.

The dispersion process was investigated in pure clays and in the presence of soda Na_2CO_3 (Table 2).

A higher degree of dispersion has been registered in nontronite clay (of the montmorillonite clay group) from the Gorodishchenskoe deposit. This parameter is somewhat

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TABLE 1

Material	Mass content, %								
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	calcination loss
Clay:									
Gorodishchenskoe	2.4	1.6	67.2	11.8	4.7	0.8	2.7		8.8
Lukoshkinskoe	0.7	0.4	69.3	17.0	3.1	0.8	1.4		6.9
Veselovskoe (VGP)	0.3	0.5	59.7	24.9	0.9	1.1	0.2	1.7	9.0
Veselovskoe (VGO)	0.5	0.6	53.7	32.1	0.6	0.5	0.7	2.0	9.1
Kaolin:									
Glukhovetskoe	0.8	0.2	47.0	36.9	0.4	0.6	0.2	0.2	13.7
Prosyanovskoe	0.6	0.3	49.6	34.9	0.5	0.4	0.2	1.0	12.5

TABLE 2

Material and treatment conditions	Average particle diameter, μm	Dispersion coefficient
Lukoshkinskoe clay:		
initial	2.07	–
after autoclave treatment	1.86	1.11
the same with 0.5% soda additive	1.67	1.24
Gorodishchenskoe clay:		
initial	2.67	–
after autoclave treatment	1.61	1.66
the same with 0.5% soda additive	1.74	1.53
Veselovskoe (VGO):		
initial	1.87	–
after autoclave treatment	1.67	1.12
Veselovskoe clay (VGP):		
initial	2.06	–
after autoclave treatment	1.60	1.29
Prosyanovskoe kaolin:		
initial	1.60	–
after autoclave treatment	1.54	1.04
Glukhovetskoe kaolin:		
initial	1.73	–
after autoclave treatment	1.53	1.13

lower in kaolinite-hydromica clays, which include clays from the Lukoshkinskoe and Veselovskoe (VPG) deposits. The lowest degree of dispersion was observed in Veselovskoe clay BGO and in kaolins. This may be related to their structure and, in the case of kaolins, to their technological prehistory (moist concentration) as well.

The determination of dispersion of argillaceous particles is currently regulated by GOST 21216.2–81, using the microaggregate method to prepare argillaceous materials for analysis, including boiling clay for 1 h in a sodium pyrophosphate solution. This method is similar to autoclave treatment in its effect on the material.

Thus, it can be stated that dispersion of argillaceous materials depends on their technological prehistory, mineralogical composition, and structural instability.

The hydrothermal stabilization of the structure of argillaceous materials can be effectively used in ceramics technology. It was proposed in [5] to replace the technological stage of drying by pressurized steam treatment. It should be stressed that the authors studying the autoclave treatment of materials considered only two important processes, namely, the formation of calcium hydrosilicates and drying, without taking into account possible structural modifications of argillaceous minerals.

The results of studying the effect of autoclave stabilization on the process of firing and on the physicomechanical characteristics of the product in the present study are given for two most intensely dispersing clays: Gorodishchenskoe and Lukoshkinskoe clays. In some cases clay was mixed with additives before steaming. These additives, apart from soda, included dust generated by the Oskol'skii Electric Steel-melting Works (OESW) that had the following composition (wt.%): 74.5 iron oxides converted to Fe_2O_3, 9.2 CaO, 5.2 MgO, 5.2 SiO_2, and 2.0 MnO. This dust was introduced with simultaneous milling of the components and Na_2CO_3 was added in the form of 10% aqueous solution. Both initial and stabilized materials were used to mold cylindrical samples of height and diameter 30 mm using semidry molding (moisture about 6%) and pressing pressure 30 MPa. The results of physicochemical testing of samples after firing are listed in Table 3.

The autoclave stabilization of the structure of argillaceous materials improved the physicomechanical properties of ceramic samples. The fire shrinkage in samples of Gorodishchenskoe clays, which is the most sensitive to structural modifications, decreases after preliminary steam treatment. The fire shrinkage in Lukoshkinskoe clay does not vary, but its water absorption grows to some extent. Such behavior in sintering of the more disperse clays subjected to steaming may be related to a structural stabilization of the materials. The strength characteristics of ceramics made from autoclave-treated clay are higher. All this may be evidence of the firing processes proceeding in more stable conditions [1]. An increase in firing temperature, if admissible, decreases the effect of nonequilibrium of the processes in firing on the structure (presumably relaxation processes take place and decrease the stresses in the articles) and, accordingly, on the physicomechanical properties of ceramics (Table 3, samples 1, 2 and 7, 8).

Of special interest are experiments in the simultaneous use of autoclave stabilization of clay and a mineralizing agent represented by Na_2CO_3 and by dust from electric steel-melting production. The soda additive has a significant

TABLE 3

Sample	Composition, %			Steaming	Firing temperature, °C	Fire shrinkage, %	Density, kg/m^3	Water absorption, %	Compressive strength, MPa
	clay	dust from OESW	Na_2CO_3 (above 100%)						
				Gorodishchenskoe clay					
1	100	–	–	–	920	1.44	1880	14.7	18.9
2	100	–	–	+	920	0.67	1910	12.3	36.0
3	99	1	0.5	+	920	1.33	1990	9.9	48.9
4	98	2	0.5	+	920	1.66	1950	11.3	32.3
5	99	1	–	+	920	1.66	1960	11.0	36.3
6	98	2	–	+	920	1.66	1990	11.0	38.4
7	100	–	–	–	960	3.33	1970	5.0	39.2
8	100	–	–	+	960	2.56	1990	8.3	41.6
9	100	–	0.5	+	960	2.56	2000	7.8	55.5
				Lukoshkinskoe clay					
10	100	–	–	–	1050	3.30	2170	8.3	35.6
11	100	–	–	+	1050	3.30	2130	9.8	42.1
12	100	–	0.5	–	1050	3.30	2130	8.8	42.8
13	100	–	0.5	+	1050	3.30	2130	9.1	54.8
14	95	5	0.5	–	1050	5.00	2260	6.0	63.0
15	95	5	0.5	+	1050	5.70	2310	4.2	97.0

effect on the structural modifications at the stage of autoclave treatment (Table 2). Thus, for Lukoshkinskoe clay a combination of dust, soda, and steam treatment increased the strength parameters more than 1.7 times, with the water absorption decreasing by half compared to the initial clay (Table 3, samples 10 and 15).

The structural stabilization can be even more effective in materials obtained by the casting technology. To prepare a ceramic suspension with stable parameters and to improve its casting and flow properties, it is recommended to age the prepared slip for 3 – 5 days. The reaction of substitution of electrolyte sodium for adsorbed calcium ions and the dispersion of argillaceous aggregates with maturing of the suspension proceed more completely, which facilitates better thinning of the ceramic mixture and a more complete moisture removal during casting in gypsum molds. The mass increment rate in this case grows, the residual moisture of the cast preform decreases, and the strength of the molded preform grows perceptibly.

The autoclave treatment in this case makes it possible not only to stabilize the structure of the material, but the composition of the slip as well. Thus, calcium hydroxide, which is frequently present in concentrated kaolin in these conditions, reacts with aluminosilicates and its impact on the slip rheology becomes weaker.

Our studies were performed on slip for sanitaryware. We used a relatively stable argillaceous material containing (%): 13 Veselovskoe clay VGP, 9 Veselovskoe clay VGO, 4 Latnenskoe clay LT-1, 25 Glukhovetskoe kaolin, and 3 Prosyanovskoe kaolin. The rest were pegmatite, quartz sand, breakage, and electrolyte additives, The pegmatite, quartz sand, and broken ceramics were prepared by dry milling. The argillaceous materials were obtained by liquefying in a fast rotor mixer. A reference slip was prepared from nontreated raw components, whereas for the experimental slip all argillaceous components were subjected to autoclave treatment for 6 h with a steam pressure of 1.0 MPa. The slip prepared from autoclave-treated clay materials exhibited a constancy of properties directly after its preparation. Thus, the slip thickening coefficient varied by 0.9% in 24 h, whereas in the reference slip this variation was at least 5% even after several days of aging. This technique is presumably effective for productions involving materials with unstable structure and properties.

Thus, the structural instability of argillaceous materials can have a perceptible effect on the properties of molding mixtures and finished ceramic products, whereas a controlled formation of properties of the materials at the stage of pretreatment reduces the degree of nonequilibrium of the processes in firing and ensures a better quality of the end product.

REFERENCES

1. V. S. Bakunov and A. V. Belyakov, “Prospects for improving the reproducibility of the structure and properties of ceramics,” *Ogneup. Tekh. Keram.*, No. 2, 16 – 21 (1998).
2. V. S. Lesovik, *A Decrease in Power Consumption in Production of Construction Materials Taking into Account the Genesis of Rocks, Author’s Abstract of Doctoral Thesis* [in Russian], Moscow (1977).
3. P. G. Komokhov, A. P. Komokhov, and V. A. Chernakov, “The mechanism of structure formation in dispersed aluminosilicates,” *Tsement*, No. 6, 22 – 29 (1992).
4. V. I. Mikitchuk, *Improving Quality of Wall Ceramics* [in Russian], Budivel’nik, Kiev (1980).
5. P. I. Bozhenov, I. V. Glibina, and B. A. Grigor’ev, *Construction Ceramics from Industrial Byproducts* [in Russian], Stroiizdat, Moscow (1986).
6. P. P. Budnikov, “The reaction between kaolin and calcium oxide hydrate under hydrothermal treatment,” in: *Proc. Conf. on Chemistry of Concrete* [in Russian], Moscow (1956), pp. 294 – 303.